CHEMICAL LOOPING COMBUSTION OF CHARCOAL WITH CALCIUM MODIFIED IRON-BASED OXYGEN CARRIERS FOR REDUCE EMISSION OF AIR POLLUTANTS NO_X AND SO_2

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Chemical looping combustion was conducted in a moving bed reactor with two kinds of an iron source as a reactive phase in oxygen carriers and modification with $Ca(OH)_2$ was used to enhance reactivity with fuels. In the moving bed reactor, calcium modified electric arc furnace slag (EAF-slag)/Al_2O_3 and calcium modified iron oxide powder (Fe_2O_3)/Al_2O_3 were selected as oxygen carriers. The air pollutant analysis indicated that the emission of NO_x and SO_2 were very low for both Ca-modified iron-based oxygen carriers, which implies that the chemical looping combustion process could reduce emission of air pollutants. Calcium Modification, Chemical Looping Process, Iron-based Oxygen Carriers, Moving Bed Fuel Reactor

I. INTRODUCTION

Oxygen carriers are viewed as the cornerstone of chemical looping technology. Most of the oxygen carriers in previous reports were focus on synthesized materials and mineral substances. Chen et al. (2017) indicated that the performance of iron-based oxygen carriers for the solid-fueled CLC could be improved by introducing the amount of alkali or alkaline earth metals [1]. Therefore, the preparation of both iron-based oxygen carriers were added different materials, such as Al_2O_3 and $Ca(OH)_2$. A moving bed reactor was used to assess the performance of charcoal combustion with Ca-Fe_2O_3/Al_2O_3 and Ca-EAF-slag/Al_2O_3 oxygen carriers, and some operating parameters, such as reaction temperature, gasification agents flow rate and oxygen carriers flow rate were discussed. Furthermore, a air pollutant analysis was carried out, and the concentration of NO_x and SO_2 were discussed.

II. EXPERIMENTAL

A. Preparation of Iron-Based Oxygen Carriers

In order to increase the performance of oxygen carriers such as reactivity, mechanical strength and attrition, Al_2O_3 and $Ca(OH)_2$ were added into iron-based oxygen carriers. The well-mixed iron-based slurry was dried at 130 °C for 8 h to form particles. The oxygen carriers was subsequently pulverized and sieved to obtain the desired particle size between 1.2-1.4 mm. Subsequently, iron-based oxygen carriers were calcined at 1300 °C for 2 h at air atmosphere in a muffle furnace.

B. Moving bed fuel reactor for using the BC-charcoal in chemical looping combustion

The annular dual-tube moving bed fuel reactor system is composed of a fuel reactor, two screw conveyors for oxygen carriers transport, two oxygen carriers holders, one screw conveyor for solid fuels transport and one solid fuels holder. The reactor is covered by an electrical heating element to provide isothermal atmosphere. The electric heater temperature is controlled by PID temperature controllers with three K-type thermocouples. The nitrogen carrier gas flow is controlled using the mass flow controller. Steam flow rate is controlled using the syringe pump. The outlet stream from the reactor is cooled down by a cooling unit to condense the vapor, and the stream is analyzed with a gas chromatography equipped with a thermal conductivity detector (GC-TCD, China Chromatography 2000) to detect carbon dioxide, carbon monoxide, methane and oxygen are measured by NDIR (Jusun).

III. RESULTS AND DISCUSSION

Owing to the existence of nitrogen and sulfur in fuel, the emission of fuel-NO_x and SO_2 were significant concern during the chemical looping combustion process. In this section, the air pollutant analysis in chemical looping combustion was conducted in the moving bed reactor at 900 °C by feeding charcoal at flow rate of 1.05 g/min, oxygen carriers at flow rate of 8.97 g/min and steam at flow rate of 157.7 mmol/min. The concentration of NO_x and SO_2, which were detected by portable emission analyzer were compared with the theoretical calculated value. The theoretical calculation for NO_x and SO_2 emission were determined on the base of the reaction between the oxygen carriers and fuel [2],[3], which was described as reaction (1).

Reaction (1):

$$C_{6.95}H_{2.11}O_{0.16}N_{0.06}S_{0.003} + 39.64Fe_2O_3 \rightarrow 6.95CO_2 + 1.055H_2O + 0.06NO + 0.003SO_2 + 26.42Fe_3O_4$$

A.20% Ca-Fe2O3/Al2O3 oxygen carriers

A.1 NO_x release curves

Figure 1 shows the NO_x release curves during

chemical looping combustion in moving bed reactor at 900 °C. It clearly reflected the whole CLC process, at the reduction stage, the charcoal was converted with NO_x released slowly due to the char gasification and the subsequent oxidization of gasification products by oxygen carrier. NO_x emission in this period exhibited a low concentration, which was lower than the theoretical calculated values, as shown in Figure 1. It indicated that the major nitrogenated species observed in the flue gas was N_2. There was only 1.5% of the N exiting from the flue gas was as NO_x after reaction conducted 100 seconds, the same result was also reported by Mendiara et al. (2014) [4]. It could be due to a reductive atmosphere in the iG-CLC process that promoted the reduction of NO to N_2.

A.2 SO2 release curves

The SO_2 emission during chemical looping combustion in moving bed reactor was shown in Figure 2. The concentration of SO_2 remained zero, which implied there was no SO_x emission in the flue gas. It also shown the expected SO_2 emission in Figure 2, which was calculated from theoretical calculated values [5]. It could be observed that calculated SO_2 emission was much higher than the measured ones.
This could be caused by the sulfur reacting with Ca or Fe in the oxygen carriers and then was transferred to leave the reactor by screw conveyor. The SEM-EDX analysis was conducted to investigate the surface of reduced-oxygen carriers [6].

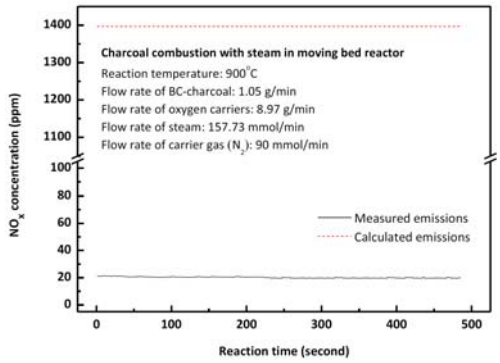


Fig. 1. NO_x variations during chemical looping combustion in moving bed reactor with 20% Ca-Fe_2O_3/Al_2O_3 oxygen carriers.

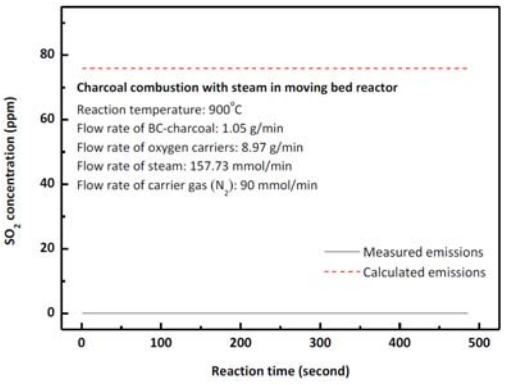


Fig. 2. SO_2 variations during chemical looping combustion in moving bed reactor with 20% Ca-Fe_2O_3/Al_2O_3 oxygen carriers.

B. 20% Ca-EAF-slag/Al_2O_3 oxygen carriers

B.1 NO_x release curves

The emission of NO_x in the flue gas was presented in Figure 3. The NO_x release during the chemical looping combustion process concentrated on the initial volatile-N release stage, showed similar trend and exhibited little differences compared to the NO_x emission with 20% Ca-Fe_2O_3/Al_2O_3 oxygen carriers. The NO_x concentration obtained in this section was nearly 22 ppm, was slightly higher than 20 ppm which was the NO_x emission with 20% Ca-Fe_2O_3/Al_2O_3 oxygen carriers in chemical looping combustion process. It could be attributed to the relatively high charcoal conversion by 20% Ca-EAF-slag/Al_2O_3 oxygen carriers.

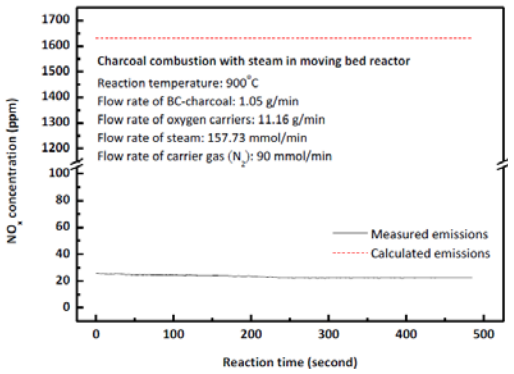


Fig. 3. NO_x variations during chemical looping combustion in moving bed reactor with 20% Ca-EAF-slag/Al_2O_3 oxygen carriers.

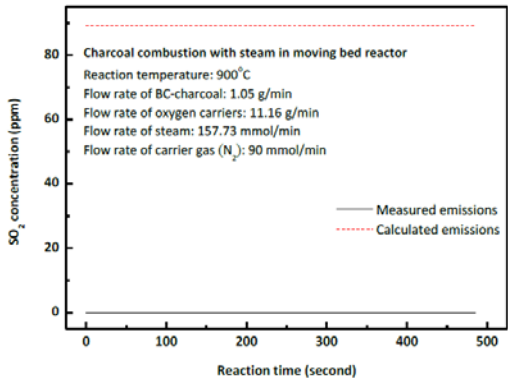


Fig. 4. SO_2 variations during chemical looping combustion in moving bed reactor with 20% Ca-EAF-slag/Al_2O_3 oxygen carriers.

B.2 SO_2 release curves

The SO_2 emission during chemical looping combustion process was remained zero and lower than the theoretical calculated values [5], as shown in Figure 4, which implied the SO_2 could be reduced by the oxygen carriers. The SEM-EDX analysis was conducted to investigate the surface of reduced-oxygen carriers. Figure 5 (a)and(b) shows that there was small amount of sulfur presented on the surface of oxygen carriers. Therefore, the SO_2 emission from charcoal combustion would decrease by oxygen carriers [6].

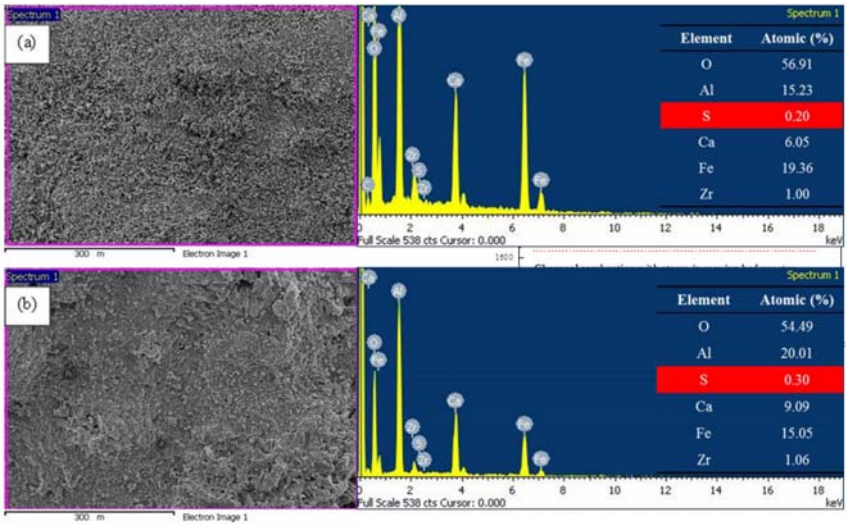


Fig. 5. SEM-DEX analysis of reduced (a) 20% Ca-Fe2O3/Al2O3 oxygen carriers and (b) 20% Ca-EAF-slag/Al2O3 oxygen carriers.

CONCLUSIONS

A analysis of air pollutant was conducted for charcoal combustion with two kinds of Ca-modified iron based oxygen carriers. The results indicated that most of the nitrogen-containing species released in the CLC process was N_2 and only 1.5% nitrogen-containing species released were NO_x for both oxygen carriers. Moreover, there was no SO_2 emission obtained for both oxygen carriers during the charcoal combustion. It could be concluded that the emission of air pollutant could be reduced using chemical looping process for charcoal combustion. The EAF-slag from steel production was successfully applied as iron source to produce the oxygen carriers, and its combustion performance during chemical looping process was better than another oxygen carrier which was produced using commercial iron oxide power as iron source. The results implied that industrial waste could be another potential iron source of oxygen carriers due to the low cost, environmentally friendly, and accessible in large quantities, compared to commercial iron oxide power as iron source of oxygen carriers.

RECOMMENDATIONS

According to the experimental results, some recommendations could be suggested for further study as follows:

1. A different solid fuel, such as biomass and petroleum coke could be applied in the chemical looping combustion with Ca-modified iron based oxygen carriers.
2. The chemical looping gasification process could be investigated with Ca-modified iron based oxygen carriers, which implied the main product in flue gas should be syngas instead of carbon dioxide.
3. The particle size of charcoal could be minified in order to increase the fuel conversion.

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